

THE CLAIMS

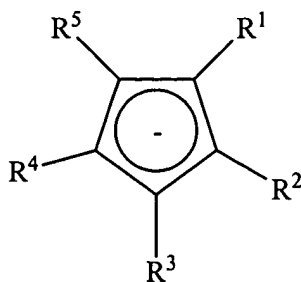
What is claimed is:

1. A method for depositing a ruthenium thin film onto a substrate, said method comprising:

 (a) depositing a nucleation layer comprising ruthenium onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited using a nucleation layer mixture under nucleation layer CVD conditions; and

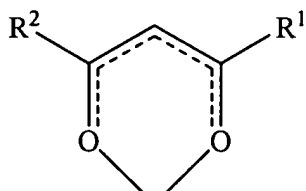
 (b) depositing an upper layer comprising ruthenium onto the nucleation layer by chemical vapor deposition, wherein the upper layer is deposited using an upper layer mixture under upper layer CVD conditions.
2. The method of claim 1, wherein the nucleation layer comprises ruthenium oxide.
3. The method of claim 1, wherein the nucleation layer CVD conditions comprise temperature in a range of about 250°C and about 340°C.
4. The method of claim 1, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 8 Torr.
5. The method of claim 4, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.4 Torr to about 1.6 Torr.
6. The method of claim 1, wherein the nucleation layer mixture comprises a first ruthenium precursor, a first co-reactant gas, and optionally a first inert gas.

7. The method of claim 6, wherein the first ruthenium precursor comprises a solid.
8. The method of claim 6, wherein the first ruthenium precursor comprises a liquid.
9. The method of claim 6, wherein the first ruthenium precursor is dissolved in a solvent to form a first ruthenium precursor solution.
10. The method of claim 9, wherein the solvent comprises a reducing solvent.
11. The method of claim 6, wherein the nucleation layer mixture comprises the first co-reactant gas at a concentration of about 80 mole% to about 95 mole%, based on the total number of moles of the nucleation layer mixture.
12. The method of claim 6, wherein the first co-reactant gas comprises oxygen.
13. The method of claim 6, wherein the first ruthenium precursor comprises a ruthenium compound selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
14. The method according to claim 13, wherein the ruthenocenes have the formula $(Cp')Ru(Cp'')$, where Cp' and Cp'' can be same or different and have the general formula:



where R¹ - R⁵ are independently selected from the group consisting of H, F, and straight-chained or branched C₁ - C₅ alkyl groups.

16. The method of claim 13, wherein the ruthenocene comprises Ru(EtCp)₂ or Ru(Cp)₂.
17. The method according to claim 13, wherein the ruthenium β-diketonates have the formula Ru(β-diketonate)₃, where β-diketonate has the general formula:



where R¹ and R² are independently selected from the group consisting of H, F, straight-chained or branched C₁ - C₅ alkyl groups, and fluorine-substituted straight-chained or branched C₁ - C₅ alkyl groups.

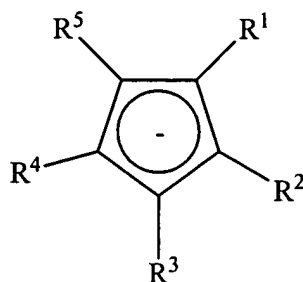
18. The method of claim 13, wherein the ruthenium β-diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium (Ru(acac)₃); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium (Ru(tfac)₃); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium (Ru(thd)₃);

tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium (Ru(hfac)₃);
 tris(2,2,7-tetramethyl-3,5-octanedionato) ruthenium (Ru(tod)₃);
 tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ruthenium
 (Ru(fod)₃); and tris(2,4-octanedionato) ruthenium (Ru(od)₃).

19. The method of claim 13, wherein the ruthenium β -diketonate comprises Ru(thd)₃ or Ru(hfac)₃.
20. The method of claim 6, wherein the rate of introduction of the first ruthenium precursor is in a range of about 15 $\mu\text{mol}/\text{min}$ to about 30 $\mu\text{mol}/\text{min}$.
21. The method of claim 1, wherein the substrate comprises a substrate material selected from the group consisting of silicon, silicon dioxide, silicon nitride, hafnium silicon oxide, hafnium silicon oxynitride, Co(WP), copper, titanium nitride, titanium aluminum nitride, tantalum nitride, tantalum pentaoxide, barium strontium titanate and lead zirconate titanate.
22. The method of claim 1, wherein the resistivity of the nucleation layer is less than about 250 $\mu\Omega\text{-cm}$.
23. The method of claim 1, wherein the rate of deposition of the nucleation layer is in a range of about 5 $\text{\AA}/\text{min}$ to about 1 $\text{\AA}/\text{min}$.
24. The method of claim 7, wherein delivery of the nucleation layer mixture to a chemical vapor deposition chamber is by solid delivery approach.
25. The method of claim 24, further comprising the separate addition of a solvent to the solid delivery approach.

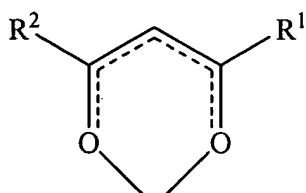
26. The method of claim 8, wherein delivery of the nucleation layer mixture to the chemical vapor deposition chamber is by liquid delivery approach.
27. The method of claim 1, wherein the upper layer consists essentially of ruthenium.
28. The method of claim 1, wherein the upper layer CVD conditions comprise temperature in a range of about 280°C and about 400°C.
29. The method of claim 1, wherein the upper layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 2 Torr.
30. The method of claim 29, wherein the upper layer CVD conditions comprise pressure in a range of about 0.4 Torr to about 1.0 Torr.
31. The method of claim 1, wherein the upper layer mixture comprises a second ruthenium precursor, a second co-reactant gas, and optionally a second inert gas.
32. The method of claim 31, wherein the second ruthenium precursor comprises a solid.
33. The method of claim 31, wherein the second ruthenium precursor comprises a liquid.
34. The method of claim 31, wherein the second ruthenium precursor is dissolved in a solvent to form a second ruthenium precursor solution.

35. The method of claim 34, wherein the solvent comprises a reducing solvent.
36. The method of claim 35, wherein the solvent comprises tetrahydrofuran (THF).
37. The method of claim 31, wherein the upper layer mixture comprises the second co-reactant gas at a concentration of about 1 mole% by weight to about 10 mole%, based on the total number of moles of the upper layer mixture.
38. The method according to claim 31, wherein the second co-reactant gas comprises oxygen.
39. The method according to claim 31, wherein the second co-reactant gas comprises an oxygen:hydrogen gas mixture.
40. The method of claim 39, wherein the oxygen:hydrogen gas mixture has a ratio in a range of about 1:1 to about 1:3.
41. The method of claim 31, wherein the second ruthenium precursor comprises a ruthenium compound selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
42. The method according to claim 41, wherein the ruthenocenes have the formula $(Cp')Ru(Cp'')$, where Cp' and Cp'' can be same or different and have the general formula:



where R¹ - R⁵ are independently selected from the group consisting of H, F, and straight-chained or branched C₁ - C₅ alkyl groups.

43. The method according to claim 41, wherein the ruthenocene comprises Ru(EtCp)₂ or Ru(Cp)₂,
44. The method according to claim 41, wherein the ruthenium β-diketonates have the formula Ru(β-diketonate)₃, where β-diketonate has the general formula:



where R¹ and R² are independently selected from the group consisting of H, F, straight-chained or branched C₁ - C₅ alkyl groups, and fluorine-substituted straight-chained or branched C₁ - C₅ alkyl groups.

45. The method of claim 41, wherein the ruthenium β-diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium (Ru(acac)₃); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium (Ru(tfac)₃); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium (Ru(thd)₃);

tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium (Ru(hfac)₃);
 tris(2,2,7-tetramethyl-3,5-octanedionato) ruthenium (Ru(tod)₃);
 tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ruthenium
 (Ru(fod)₃); and tris(2,4-octanedionato) ruthenium (Ru(od)₃).

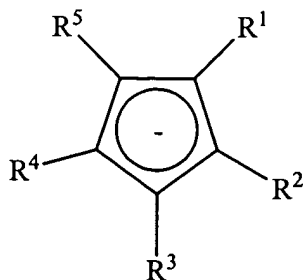
46. The method of claim 41, wherein the ruthenium β -diketonate comprises Ru(thd)₃ or Ru(hfac)₃.
47. The method of claim 31, wherein the rate of introduction of the second ruthenium precursor is in a range of about 5 $\mu\text{mol/min}$ to about 20 $\mu\text{mol/min}$.
48. The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 8 $\mu\Omega\text{-cm}$ to about 25 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 10.0 nm to about 35.0 nm thick.
49. The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 12 $\mu\Omega\text{-cm}$ to about 25 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 5.0 nm to about 15.0 nm thick.
50. The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 20 $\mu\Omega\text{-cm}$ to about 125 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 2.0 nm to about 5.0 nm thick.
51. The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 10 $\mu\Omega\text{-cm}$ to about 100 $\mu\Omega\text{-cm}$.

52. The method of claim 1, wherein the thickness of the ruthenium thin film is in a range of about 25 Å to about 350 Å.
53. The method of claim 1, wherein the rate of deposition of the upper layer is in a range of about 5 Å/min to about 1 Å/min.
54. The method of claim 32, wherein delivery of the upper layer mixture to the chemical vapor deposition chamber is by solid delivery approach.
55. The method of claim 54, further comprising the separate addition of a solvent to the solid delivery approach.
56. The method of claim 33, wherein delivery of the upper layer mixture to the chemical vapor deposition chamber is by liquid delivery approach.
57. The method of claim 1, further comprising annealing the nucleation layer prior to deposition of the upper layer.
58. The method of claim 1, further comprising annealing the ruthenium thin film following deposition of the upper layer on the nucleation layer.
59. The method of claim 31, wherein the second ruthenium precursor is different than the first ruthenium precursor.
60. The method of claim 1, wherein the ruthenium thin film has an impurity content of less than about 2 atomic%.

61. The method of claim 1, wherein the substrate comprises a metallic portion and a dielectric portion.
62. The method of claim 61, wherein the nucleation layer on the metallic and dielectric portions of the substrate is a peel-resistant layer film.
63. The method of claim 1, wherein the rate of deposition of the upper layer is less than a rate of surface reaction rate-limited deposition to deposit a ruthenium thin film having an impurity content of less than about 2 atomic%.
64. The method of claim 1, wherein the ruthenium thin film comprises the nucleation layer and the upper layer.
65. A method for depositing a ruthenium thin film onto a substrate, said method comprising:
 - (a) depositing a nucleation layer comprising ruthenium onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited from a nucleation layer mixture in an oxidizing environment under nucleation layer CVD conditions; and
 - (b) deoxygenating the nucleation layer comprising ruthenium in a reducing environment,wherein (a) and (b) are repeated sequentially and continuously until the ruthenium thin film of desired thickness is deposited onto the substrate.

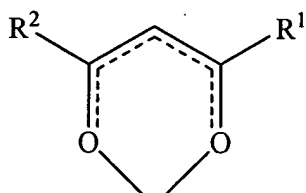
66. The method of claim 65, wherein said deoxygenating comprises exposing said nucleation layer to a gas mixture comprising a reducing agent and optionally, an inert gas.
67. The method of claim 66, wherein the reducing agent comprises hydrogen.
68. The method of claim 65, wherein the deoxygenating step is conducted under conditions comprising pressure in a range of about 0.1 Torr to about 100 Torr.
69. The method of claim 65, wherein the deoxygenating step is conducted under conditions comprising temperature in a range of about 250°C to about 350°C.
70. The method of claim 65, wherein the temporal length of deposition of the nucleation layer in step (a) is greater than the succeeding repetitions of step (a).
71. The method of claim 65, wherein the nucleation layer comprises ruthenium oxide.
72. The method of claim 65, wherein the nucleation layer CVD conditions comprise temperature in a range of about 250°C and about 340°C.
73. The method of claim 65, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 8 Torr.
74. The method of claim 65, wherein the nucleation layer mixture comprises a first ruthenium precursor, a first co-reactant gas, and optionally a first inert gas.

75. The method of claim 74, wherein the first ruthenium precursor comprises a solid.
76. The method of claim 74, wherein the first ruthenium precursor comprises a liquid.
77. The method of claim 74, wherein the first ruthenium precursor is dissolved in a solvent to form a first ruthenium precursor solution.
78. The method of claim 77, wherein the solvent comprises a reducing solvent.
79. The method of claim 78, wherein the solvent is tetrahydrofuran (THF).
80. The method of claim 74, wherein the nucleation layer mixture comprises the first co-reactant gas at a concentration of about 80 mole% to about 95 mole%, based on the total number of moles of the nucleation layer mixture.
81. The method of claim 74, wherein the first co-reactant gas comprises oxygen.
82. The method of claim 74, wherein the first ruthenium precursor comprises a ruthenium compound selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
83. The method according to claim 82, wherein the ruthenocenes have the formula $(Cp')Ru(Cp'')$, where Cp' and Cp'' can be same or different and have the general formula:



where R¹ - R⁵ are independently selected from the group consisting of H, F, and straight-chained or branched C₁ - C₅ alkyl groups.

84. The method according to claim 82, wherein the ruthenocene comprises Ru(EtCp)₂ or Ru(Cp)₂,
85. The method according to claim 82, wherein the ruthenium β-diketonates have the formula Ru(β-diketonate)₃, where β-diketonate has the general formula:



where R¹ and R² are independently selected from the group consisting of H, F, straight-chained or branched C₁ - C₅ alkyl groups, and fluorine-substituted straight-chained or branched C₁ - C₅ alkyl groups.

86. The method of claim 82, wherein the ruthenium β-diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium (Ru(acac)₃); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium (Ru(tfac)₃); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium (Ru(thd)₃);

tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium (Ru(hfac)_3);
 tris(2,2,7-tetramethyl-3,5-octanedionato) ruthenium (Ru(tod)_3);
 tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ruthenium
 (Ru(fod)_3); and tris(2,4-octanedionato) ruthenium (Ru(od)_3).

87. The method of claim 82, wherein the ruthenium β -diketonate comprises Ru(thd)_3 or Ru(hfac)_3 .
88. The method of claim 74, wherein the rate of introduction of the first ruthenium precursor is in a range of about 15 $\mu\text{mol/min}$ to about 30 $\mu\text{mol/min}$.
89. The method of claim 65, wherein the substrate comprises a substrate material selected from the group consisting of silicon, silicon dioxide, silicon nitride, hafnium silicon oxide, hafnium silicon oxynitride, Co(WP), copper, titanium nitride, titanium aluminum nitride, tantalum nitride, tantalum pentaoxide, barium strontium titanate and lead zirconate titanate.
90. The method of claim 65, wherein the resistivity of the nucleation layer is less than about 250 $\mu\Omega\text{-cm}$.
91. The method of claim 65, wherein the rate of deposition of the nucleation layer is in a range of about 5 \AA/min to about 1 \AA/min .
92. The method of claim 65, wherein the resistivity of the ruthenium thin film is in a range of about 15 $\mu\Omega\text{-cm}$ to about 50 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 3.0 nm to about 10.0 nm.

93. The method of claim 65, wherein the resistivity of the ruthenium thin film is in a range of about $15\ \mu\Omega\text{-cm}$ to about $30\ \mu\Omega\text{-cm}$, and has a thickness in a range of from about 4.0 nm to about 8.0 nm.
94. The method of claim 65, wherein delivery of the nucleation layer mixture to the chemical vapor deposition chamber is by solid delivery approach.
95. The method of claim 94, further comprising the separate addition of a solvent to the solid delivery approach.
96. The method of claim 65, wherein delivery of the nucleation layer mixture to the chemical vapor deposition chamber is by liquid delivery approach.